

Van der Waals Interactions in DFT using Wannier Functions: improved C_6 and C_3 coefficients by a new approach

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A new implementation is proposed for including van der Waals interactions in Density Functional Theory using the Maximally-Localized Wannier functions. With respect to the previous DFT/vdW-WF method, the present DFT/vdW-WF2 approach, which is based on the simpler London expression and takes into account the intrafragment overlap of the localized Wannier functions, leads to a considerable improvement in the evaluation of the C_6 van der Waals coefficients, as shown by the application to a set of selected dimers. Preliminary results on Ar on graphite and Ne on the Cu(111) metal surface suggest that also the C_3 coefficients, characterizing molecule-surfaces van der Waals interactions are better estimated with the new scheme.

An accurate description of ubiquitous, long-range van der Waals (vdW) interactions is crucial for characterizing countless phenomena, belonging to such diverse fields as solid state and surface physics, chemistry and biology. For instance, vdW effects are responsible for the stabilization of non covalently-bonded crystals and layered structures, play a major role in physisorption processes, and are known to affect several biological phenomena. vdW interactions are due to long range-correlations, in particular, the leading R^{-6} term is a consequence of correlated, instantaneous dipole fluctuations. Density Functional Theory (DFT), thanks to its favorable scaling properties, represents a popular, efficient and invaluable approach, that is also applicable to extended systems where other ab initio schemes turn out to be too computationally expensive. However, standard DFT schemes only provide a local or semilocal treatment of the electronic correlation, so that they are unable to properly reproduce genuine vdW effects.¹

The simplest way to include vdW interactions in DFT is represented by semiempirical methods,^{2,3} where, typically, an approximately derived C_6/R^{-6} term is multiplied by a short-range damping function, with parameters tailored to the specific system considered. Although such an approach is very efficient and often gives a substantial improvement with respect to a standard DFT method, nonetheless its accuracy is difficult to assess in advance and lacks of transferability (for instance, changes in atomic polarizabilities by changing the atom environment are neglected). Clearly, better reliability, accuracy, and transferability can be in principle achieved by adopting schemes where vdW corrections are computed by exploiting the knowledge of the electronic density distribution given by DFT. In recent years several approaches have been indeed proposed (for a recent review, see, for instance, ref. 4) In order to circumvent the direct use of truly non-local DFT functionals, which are not easy to evaluate efficiently, some of these methods introduce suitable partitioning schemes into separated interacting fragments, either relying on effective atom-atom⁵⁻⁷ or electronic orbital-orbital⁸⁻¹¹ pairwise C_6/R^6 terms. Although these techniques are expected to be more reliable

and transferable than semiempirical approaches, in practice, most of them use one or more parameters to be fitted using some reference database.

Here we describe and apply a new implementation of the DFT/vdW-WF method^{8,9,11,12} where electronic charge partitioning is achieved using the Maximally-Localized Wannier Functions (MLWFs). The MLWFs are obtained from a unitary transformation in the space of the occupied Bloch states, by minimizing the total spread functional:¹³

$$\Omega = \sum_n S_n^2 = \sum_n \left(\langle w_n | r^2 | w_n \rangle - \langle w_n | \mathbf{r} | w_n \rangle^2 \right). \quad (1)$$

The localization properties of the MLWFs are of particular interest for the implementation of an efficient vdW correction scheme: in fact, the MLWFs represent a suitable basis set to evaluate orbital-orbital vdW interaction terms. While in the original DFT/vdW-WF method the vdW energy correction for two separate fragments was computed using the exchange-correlation functional proposed by Andersson *et al.*,¹⁴ our novel version (DFT/vdW-WF2 method) is instead based on the simpler, well known London's expression:¹⁵ basically, two interacting atoms, A and B , are approximated by coupled harmonic oscillators and the vdW energy is taken to be the change of the zero-point energy of the coupled oscillations as the atoms approach; if only a single excitation frequency is associated to each atom, ω_A , ω_B , then

$$E_{vdW}^{London} = -\frac{3e^4}{2m^2} \frac{Z_A Z_B}{\omega_A \omega_B (\omega_A + \omega_B)} \frac{1}{R_{AB}^6} \quad (2)$$

where $Z_{A,B}$ is the total charge of A and B , and R_{AB} is the distance between the two atoms (e and m are the electronic charge and mass). Now, adopting a simple classical theory of the atomic polarizability, the polarizability of an electronic shell of charge eZ_i and mass mZ_i , tied to a heavy undeformable ion can be written as

$$\alpha_i \simeq \frac{Z_i e^2}{m \omega_i^2}. \quad (3)$$

Then, given the direct relation between polarizability and atomic volume,¹⁶ we assume that $\alpha_i \sim \gamma S_i^3$, where γ is a proportionality constant, so that the atomic volume is expressed in terms of the MLWF spread, S_i . Rewriting eq. (2) in terms of the quantities defined above, one obtains an explicit expression (much simpler than the multidimensional integrals involved in the Andersson functional¹⁴) for the C_6 vdW coefficient:

$$C_6^{AB} = \frac{3}{2} \frac{\sqrt{Z_A Z_B} S_A^3 S_B^3 \gamma^{3/2}}{(\sqrt{Z_B} S_A^{3/2} + \sqrt{Z_A} S_B^{3/2})}. \quad (4)$$

The constant γ can then be set up by imposing that the exact value for the H atom polarizability ($\alpha_H = 0.866$ a.u.) is obtained (of course, in the H case, one knows the exact analytical spread, $S_i = S_H = \sqrt{3}$ a.u.). Note that, by expressing the "atomic" volume as a function of S_i we actually implicitly switch from an atom-atom to an orbital-orbital approach.

In order to achieve a better accuracy, one must properly deal with *intrafragment* MLWF overlap: in fact, the DFT/vdW-WF method is strictly valid for nonoverlapping fragments only; now, while the overlap between the MLWFs relative to separated fragments is usually negligible for all the fragment separation distances of interest, the same is not true for the MLWFs belonging to the same fragment, which are often characterized by a significant overlap. This overlap affects the effective orbital volume, the polarizability, and the excitation frequency (see eq. (3)), thus leading to a quantitative effect on the value of the C_6 coefficient. We take into account the effective change in volume due to intrafragment MLWF overlap by introducing a suitable reduction factor ξ obtained by interpolating between the limiting cases of fully overlapping and non-overlapping MLWFs. In particular, since in the present DFT/vdW-WF2 method the i -th MLWF is approximated with a homogeneous charged sphere of radius S_i , then the overlap among neighboring MLWFs can be evaluated as the geometrical overlap among neighboring spheres. To derive the correct volume reweighting factor for dealing with overlap effects, we first consider the limiting case of two pairs (one for each fragment) of completely overlapping MLWFs, which would be, for instance, applicable to two interacting He atoms if each MLWF just describes the density distribution of a single electron; then we can evaluate a single C_6 coefficient using eq. (4) with $Z_{A,B} = 2$, so that:

$$C_6^{AB} = \frac{3}{2} \frac{\sqrt{2} S_A^3 S_B^3 \gamma^{3/2}}{(S_A^{3/2} + S_B^{3/2})}. \quad (5)$$

Alternatively, the same expression can be obtained by considering the sum of 4 identical pairwise contributions

(with $Z = 1$), by introducing a modification of the effective volume in such a way to take the overlap into account and make the global interfragment C_6 coefficient equivalent to that in eq. (5). This is clearly accomplished by replacing S_i^3 in eq. (4) with ξS_i^3 , where $\xi = 1/2$. This procedure can be easily generalized to multiple overlaps, by weighting the overlapping volume with the factor n^{-1} , where n is the number of overlapping MLWFs. Finally, by extending the approach to partial overlaps, we define the *free* volume of a set of MLWFs belonging to a given fragment (in practice three-dimensional integrals are evaluated by numerical sums introducing a suitable mesh in real space) as:

$$V_{free} = \int d\mathbf{r} w_{free}(\mathbf{r}) \simeq \Delta r \sum_l w_{free}(\mathbf{r}_l) \quad (6)$$

where $w_{free}(\mathbf{r}_l)$ is equal to 1 if $|\mathbf{r}_l - \mathbf{r}_i| < S_i$ for at least one of the fragment MLWFs, and is 0 otherwise.

The corresponding *effective* volume is instead given by

$$V_{eff} = \int d\mathbf{r} w_{eff}(\mathbf{r}) \simeq \Delta r \sum_l w_{eff}(\mathbf{r}_l), \quad (7)$$

where the new weighting function is defined as $w_{eff}(\mathbf{r}_l) = w_{free}(\mathbf{r}_l) \cdot n_w(\mathbf{r}_l)^{-1}$, with $n_w(\mathbf{r}_l)$ that is equal to the number of MLWFs contemporarily satisfying the relation $|\mathbf{r}_l - \mathbf{r}_i| < S_i$. Therefore, the non overlapping portions of the spheres (in practice the corresponding mesh points) will be associated to a weight factor 1, those belonging to two spheres to a 1/2 factor, and, in general, those belonging to n spheres to a $1/n$ factor. The average ratio between the effective volume and the free volume (V_{eff}/V_{free}) is then assigned to the factor ξ , appearing in eq. (8). Although in principle the correction factor ξ must be evaluated for each MLWF and the calculations must be repeated at different fragment-fragment separations, our tests show that, in practice, if the fragments are rather homogeneous all the ξ factors are very similar, and if the spreads of the MLWFs do not change significantly in the range of the interfragment distances of interest, the ξ 's remain essentially constant; clearly, exploiting this behavior leads to a significant reduction in the computational cost of accounting for the intrafragment overlap. We therefore arrive at the following expression for the C_6 coefficient:

$$C_6^{AB} = \frac{3}{2} \frac{\sqrt{Z_A Z_B} \xi_A S_A^3 \xi_B S_B^3 \gamma^{3/2}}{(\sqrt{Z_B} \xi_A S_A^{3/2} + \sqrt{Z_A} \xi_B S_B^{3/2})}, \quad (8)$$

where $\xi_{A,B}$ represents the ratio between the effective and the free volume associated to the A -th and B -th MLWF. The need for a proper treatment of overlap effects has been also recently pointed out by Andrinopoulos *et al.*,¹¹ who however applied a correction only to very closely centred WFCs.

Finally, the vdW interaction energy is computed as:

$$E_{vdW} = - \sum_{i < j} f(R_{ij}) \frac{C_6^{ij}}{R_{ij}^6} \quad (9)$$

where $f(R_{ij})$ is a short-range damping function, which is introduced not only to avoid the unphysical divergence of the vdW correction at small fragment separations, but also to eliminate double countings of correlation effects (in fact standard DFT approaches are able to describe short-range correlations); it is defined as:

$$f(R_{ij}) = \frac{1}{1 + e^{-a(R_{ij}/R_s - 1)}}. \quad (10)$$

The parameter R_s represents the sum of the vdW radii $R_s = R_i^{vdW} + R_j^{vdW}$, with (by adopting the same criterion chosen above for the γ parameter)

$$R_i^{vdW} = R_H^{vdW} \frac{S_i}{\sqrt{3}} \quad (11)$$

where R_H^{vdW} is the literature¹⁷ (1.20 Å) vdW radius of the H atom, and, following Grimme *et al.*,² $a \simeq 20$ (the results are almost independent on the particular value of this parameter). Although this damping function introduces a certain degree of empiricism in the method, we stress that a is the only ad-hoc parameter present in our approach, while all the others are only determined by the basic information given by the MLWFs, namely from first principles calculations.

Calculations were performed using the CPMD code¹⁸ and taking, as the reference DFT GGA functional, both the PBE¹⁹ and revPBE²⁰ flavor: PBE is chosen because it represents one of the most popular GGA functionals for standard DFT simulations of condensed-matter systems, while revPBE, which usually gives results close to those obtained by a pure Hartree-Fock approach, has been used both in our previous DFT/vdW-WF calculations and also in other vdW-corrected DFT studies.^{2,21} As already pointed out elsewhere,^{12,21,22} vdW-corrected PBE calculations show a general tendency to overbinding (attributed to an overestimate of the long-range part of the exchange contribution), with equilibrium distances in reasonable agreement with reference values, while instead vdW-corrected revPBE typically overestimates the equilibrium distances but gives better estimates for the binding energies.

We stress that the computational cost of the DFT/vdW-WF2 method, although slightly increased with respect to that of the previous DFT/vdW-WF scheme, still represents a negligible additional cost if compared to that of a standard DFT calculation, thus satisfying the basic efficiency requirement.

In Table I we report the C_6 coefficients computed for a set of 18 dimolecular systems, where vdW interactions represent the dominant (or at least a significant) contribution, using our DFT/vdW-WF2 method to be compared to reference data. As can be seen, in most of the

systems the C_6 coefficient value is reduced and the overall performance is much improved with respect to the previous DFT/vdW-WF approach:⁸ in fact the *mean relative error* (MRE) is decreased from 14.1 to 0.3 %, and from 16.6 to -0.3 % with revPBE and PBE, respectively, while the corresponding reductions in the *mean absolute relative error* (MARE) are from 35.4 to 14.6 % with revPBE and from 32.8 to 10.8 % with PBE. The effect is particularly apparent in rare-gas dimers and dimolecular complexes containing benzene, which are systems where the correction factor ξ is important due to a significant overlap among MLWFs belonging to the same fragment. Clearly, one expects that this correction will be also important in large molecules and also in extended systems, characterized by relatively delocalized electronic charge distributions, corresponding to large MLWF spreads.

Note that, the typical decrease of the C_6 coefficient values obtained by the DFT/vdW-WF2 method does not necessarily lead to a reduction of the vdW energy contribution; this is clearly due to the effect of the adopted damping function, which determines the interplay between the C_6/R^{-6} vdW correction and standard DFT energy contributions. As a result, the new DFT/vdW-WF2 scheme in general predicts slightly shorter equilibrium distances, in better agreement with reference data than DFT/vdW-WF, while instead the binding energies exhibit a behavior similar to that obtained by the DFT/vdW-WF approach, basically determined by the underlying DFT GGA functional (see above comment). We also point out that, a much more accurate estimate of the C_6 coefficients allows for a better description of the vdW interactions even for interfragment distances far from the equilibrium values, which is of particular relevance, both for the applications to large systems and for Molecular Dynamics simulations.

In order to test the applicability of the present DFT/vdW-WF2 method also to extended systems, which of course represent the most interesting application field because high-quality chemistry methods are too computationally demanding, we considered both the adsorption of a single Ar atom on graphite and of a Ne atom on the Cu(111) metal surface, which represent two typical physisorption processes. In the case of Ar on graphite, calculations have been performed using the same approach followed in ref. 22, while for Ne on Cu(111) we have used the Quantum-ESPRESSO²³ ab initio package (MLWFs have been generated as a post-processing calculation using the WanT package²⁴): we modeled the substrate using a periodically-repeated hexagonal supercell, with a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure and a surface slab made of 15 Cu atoms distributed over 5 layers; the Brillouin Zone has been sampled using a $6 \times 6 \times 1$ k -point mesh.

By fitting the adatom binding energy as a function of its distance from the substrate, z , (as it is usually done²⁵ the fit has been performed by optimizing the parameters of the function: $A e^{-Bz} - C_3/(z - z_0)^3$), one can easily estimate the C_3 coefficients that characterize the adatom-surface vdW interactions. As can be seen in Ta-

ble II, although the agreement with reference C_3 data is not perfect yet (obtaining accurate C_3 coefficients represents a notorious difficult problem, see, for instance, ref. 26), nonetheless the DFT/vdW-WF2 method gives a dramatic improvement with respect to the previous DFT/vdW-WF scheme.

In conclusion, we have described and applied a new implementation of our vdW-correction method based on the Maximally-Localized Wannier functions: the DFT/vdW-WF2 approach is based on the London ex-

pression and takes into account the MLWF intrafragment overlap. The application to selected dimers and also to Ar on graphite and Ne on the Cu(111) metal surface show a substantial improvement in the long-range vdW-coefficient (C_6 and C_3) estimates. Work is in progress to achieve a similar level of improvement in equilibrium distances and binding energies: this would probably require the introduction of more sophisticated, DFT-functional dependent, damping functions.

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	DFT/vdW-WF	DFT/vdW-WF2	Ref.
H-H	7.50(8.0)	7.17(7.48)	6.38
He-He	0.57(0.62)	1.48(1.47)	1.45
Ne-Ne	4.35(4.73)	10.4(8.9)	6.35
Ne-Ar	24.9(16.9)	26.4(22.9)	19.5
Ar-Ar	92.5(93.2)	65.8(66.1)	64.3
Kr-Kr	214.0(227.0)	124.0(124.0)	131.0
Xe-Xe	618.0(621.0)	261.0(262.0)	285.9
N ₂ -N ₂	87.4(89.3)	81.2(80.5)	73.3
CO-CO	85.6(86.7)	84.8(85.1)	81.5
NH ₃ -NH ₃	67.1(88.4)	63.5(77.6)	89.03
H ₂ O-H ₂ O	35.2(35.6)	38.9(37.3)	45.29
C ₂ H ₆ -C ₂ H ₆	308.0(315.0)	298.0(300.0)	381.9
CH ₄ -CH ₄	103.0(119.0)	98.2(111.0)	129.7
C ₆ H ₆ -C ₆ H ₆	2930.0(2900)	1710.0(1710)	1722.7
C ₆ H ₆ -Ar	490.0(495.0)	333.0(334.0)	330.1
C ₆ H ₆ -H ₂ O	323.0(325.0)	252.0(256.0)	277.4
CO ₂ -CO ₂	187.0(191.0)	162.0(158.0)	158.5
NH ₃ -CO	78.5(88.6)	75.5(80.4)	90.2
MRE	14.1(16.6)%	0.3(-0.3)%	
MARE	35.4(32.8)%	14.6(10.8)%	

TABLE I: C_6 coefficients(in meV Å⁶), using the reference DFT revPBE functional (PBE in parenthesis) computed with the DFT/vdW-WF2 method, compared with those obtained by the previous DFT/vdW-WF scheme,⁸ and with reference values.²⁷⁻³⁵

	DFT/vdW-WF	DFT/vdW-WF2	Ref.
Ar-graphite	18318	2057	1210
Ne-Cu(111)	1226	589	488

TABLE II: C_3 coefficients (in $\text{meV } \text{\AA}^3$), using the reference DFT revPBE functional computed with the DFT/vdW-WF2 method, compared with those obtained by the previous DFT/vdW-WF scheme,⁸ and with reference values.³⁶